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1 Thermodynamics of sea ice phase composition revisited

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6 **Key Points:**

- 7 • Revisit sea ice phase composition from observational and theoretical sources
- 8 • Quantify uncertainties in brine salinity and mass fraction
- 9 • Propose sea ice phase equations with solid minerals that are compatible with in-
- 10 ternational standards

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11 **Abstract**

12 Pure ice, brine and solid minerals are the main contributors to sea ice mass. Constitu-
13 tional changes with salinity and temperature exert a fundamental control on sea ice phys-
14 ical, chemical and biological properties. However, current estimation methods and model
15 representations of the sea ice phase composition suffer from two limitations – in a con-
16 text of poorly quantified uncertainties. First, salt minerals are neglected. Second, for-
17 mulations are inconsistent with international standards, in particular with the Interna-
18 tional Thermodynamic Equation of Seawater (TEOS-10). To address these issues, we
19 revisit the thermodynamics of the sea ice phase composition by confronting observations,
20 theory and the usual computation methods. We find remarkable agreement between ob-
21 servations and the Gibbs-Pitzer theory as implemented in FREZCHEM, both for brine
22 salinity (RMSE=1.9 g/kg) and liquid H₂O mass fraction (RMSE=8.6 g/kg). On this ba-
23 sis, we propose expanded sea ice phase composition equations that include minerals, are
24 expressed in terms of ITS-90 temperature and absolute salinity, and are valid down to
25 the eutectic temperature (-36.2°C). These equations precisely reproduce FREZCHEM,
26 outcompeting currently used calculation techniques. We also suggest a modification of
27 the TEOS-10 seawater Gibbs function giving a liquidus curve consistent with observa-
28 tions down to the eutectic temperature without changing TEOS-10 inside its original va-
29 lidity range.

30 **1 Introduction**

31 Sea ice is composed of pure ice, liquid brine, hydrated salt minerals and gas bub-
32 bles (*Weeks and Ackley, 1986; Light et al., 2003; Hunke et al., 2011*). These multiple phases
33 render sea ice structurally, thermodynamically, biologically and chemically different from
34 freshwater ice (*Thomas, 2017*). Of all these constituents, brine is the most studied next
35 to ice (see, e.g., *Notz, 2005*), and affects the ice thermal regime and seasonal cycle of ice
36 thickness (e.g., *Untersteiner, 1961; Bitz and Lipscomb, 1999; Vancoppenolle et al., 2005;*
37 *Wiese et al., 2015*) and, in turn, the seasonal evolution of ice extent and volume (*Semt-*
38 *ner, 1984; Vancoppenolle et al., 2009; Turner and Hunke, 2015*). The chemical compo-
39 sition and fraction of brine inclusions also largely determine the suitability of the sea ice
40 biome for microbial life (*Arrigo and Sullivan, 1992; Thomas and Dieckmann, 2002*). Sea
41 ice models represent brine inclusions from highly parameterized (*Semtner, 1976*) to more
42 and more explicit approaches (e.g. *Bitz and Lipscomb, 1999; Griewank and Notz, 2013;*

43 *Turner et al.*, 2013; *Moreau et al.*, 2015), whereas biogeochemical field-based sea ice stud-
 44 ies often include brine inclusions as part of their characterization of the sea ice environ-
 45 ment (*Miller et al.*, 2015).

46 Characterizing the sea ice phase composition is not trivial: phase composition changes
 47 with temperature T and salinity S , for two reasons. First, increasing salinity depresses
 48 the freezing temperature of seawater (*Doherty and Kester*, 1974) as fewer H_2O molecules
 49 are available to freeze (*Feistel*, 2008). Second, the crystalline lattice of solid H_2O hardly
 50 incorporates any salt because of size and charge constraints (*Weeks and Ackley*, 1986;
 51 *Petrich and Eicken*, 2009). Instead salt is dissolved in small (0.01-10 mm) liquid inclu-
 52 sions or hydrated into solid minerals (*Assur*, 1958; *Perovich and Gow*, 1996; *Marion et al.*,
 53 1999; *Light et al.*, 2003). As the ice cools, brine inclusions adjust their freezing temper-
 54 ature to maintain equilibrium by shrinking, which increases their own salinity (S_{br} , also
 55 referred to as brine salinity) to values typically much larger than the bulk salinity of the
 56 ice (e.g., *Ono*, 1967). Meanwhile, more minerals precipitate and fewer liquid H_2O molecules
 57 remain, until exhaustion of all liquid at the *eutectic* point (T_e , S_e). The eutectic point
 58 indicates the salinity and temperature couple corresponding to the lowest possible sea-
 59 water freezing temperature, below which all water becomes solid. The corresponding T -
 60 S values are referred to as *eutectic* temperature (T_e) and salinity (S_e). Both are constant
 61 for given pressure and composition.

62 The sequence of precipitating minerals under cooling has long been ambiguous. This
 63 is because the two main laboratory-based studies documenting the chemical evolution
 64 of brine from freezing down to eutectic temperatures (*Gitterman*, 1937; *Nelson and Thomp-*
 65 *son*, 1954) are not in exact agreement. Such differences are attributable to varying sam-
 66 ple equilibration times: *Gitterman* used up to 4-week periods, whereas *Nelson and Thomp-*
 67 *son* used only a few hours (see *Marion et al.*, 1999, for thorough discussion). This in turn
 68 affects the mineral form into which calcium precipitates (gypsum or antarcticite) and
 69 ultimately changes T_e : -36.2°C along the *Gitterman* pathway (gypsum) and -54°C along
 70 the *Nelson & Thompson* pathway (antarcticite). The classical sea ice phase diagram (*As-*
 71 *sur*, 1958; *Petrich and Eicken*, 2009), derived from algorithmic chemical computations,
 72 is directly based on *Nelson and Thompson's* data.

73 Ambiguities in the crystallization sequence, as well as variable calculation practices,
 74 undermine the confidence in calculated brine salinity S_{br} and mass (or volume) fraction

75 of brine ϕ , the most used descriptors of sea ice constitution. In observational studies (e.g.,
 76 *Lannuzel et al.*, 2008; *Ewert and Deming*, 2013; *Miller et al.*, 2015), S_{br} and ϕ are typ-
 77 ically computed from T and S measurements, using the observation-based empirical fits
 78 of *Cox and Weeks* (1983, 1986). Modelling authors (e.g., *Griewank and Notz*, 2013; *Turner*
 79 *et al.*, 2013; *Moreau et al.*, 2015) have used simpler, more consistent but less precise ap-
 80 proaches: they specify brine salinity from T using a simple fit, either linear (*Bitz and Lip-*
 81 *scomb*, 1999) or 3rd order (*Notz and Worster*, 2009). Then brine fraction is retrieved as
 82 the ratio of bulk over brine salinity, which relies on the assumption that minerals are neg-
 83 ligible. Brine fraction and salinity are fundamental to contemporary thermodynamic for-
 84 mulations in sea ice models, because they control all material thermodynamic proper-
 85 ties (e.g., specific heat, thermal conductivity). It must be noted that all the aforemen-
 86 tionned relationships derive from the algorithmic computations of *Assur* (1958). Will-
 87 ingly or not, these implicitly assume that the *Nelson and Thompson* (1954) crystalliza-
 88 tion pathway holds.

89 Two recent developments motivate us to revisit the sea ice phase composition prob-
 90 lem. First, recent sea ice geochemical works (*Geilfus et al.*, 2013; *Butler and Kennedy*,
 91 2015; *Butler et al.*, 2016a,b, 2017) studied the precipitation of minerals in sea ice and
 92 definitely state *Gitterman's* mineral crystallization sequence as the reference equilibrium
 93 pathway. These experimental works are all excellently backed up by theoretical calcu-
 94 lations based on Pitzer equations (*Pitzer*, 1991), implemented in the FREZCHEM code
 95 (*Marion et al.*, 1999). FREZCHEM predicts the temperature of precipitation of min-
 96 erals and the composition of brine in good agreement with laboratory experiments (*Mar-*
 97 *ion et al.*, 1999; *Butler et al.*, 2016a, 2017). The consistency of FREZCHEM with high-
 98 precision measurements of seawater freezing temperature (*Doherty and Kester*, 1974)
 99 within a few mK is also striking (*Feistel*, 2008).

100 The second development motivating us to reconsider the sea ice phase composition
 101 basis is the recent implementation into Earth System model components of standard ther-
 102 modynamic descriptions of environmental fluids. Let us mention TEOS-10, the Inter-
 103 national Thermodynamic Equation of Seawater (*Feistel*, 2008; *IOC, SCOR and IAPSO*,
 104 2010), which also includes expressions for ice I_h (*Feistel and Wagner*, 2006) and humid
 105 air (*IAPWS*, 2010). TEOS-10 is now included in some ocean models (*Roquet et al.*, 2015).
 106 These new thermodynamic equations are appealing in that they blend all thermodynamic
 107 properties of the considered material in a unique thermodynamic potential (such as a

108 Gibbs function), from which all other properties can uniquely and consistently be de-
109 rived. Another advantage of such approaches as TEOS-10 is that they are based on clearly
110 defined units. Celsius degrees, following the International Temperature Scale 1990, are
111 the reference temperature units (ITS-90, *Preston-Thomas*, 1990), whereas g/kg are the
112 reference units for absolute salinity (*Millero et al.*, 2008). The sea ice thermodynamic
113 formulations currently used in Earth System models (see *Massonnet et al.*, 2012, Table
114 1) are based on physically well-founded approximations (typically from *Semtner*, 1976;
115 *Bitz and Lipscomb*, 1999). However, in contrast with TEOS-10, these formulations were
116 not built from a unique thermodynamic potential and therefore are somehow inconsis-
117 tent. In addition, they are not clear in terms of which temperature and salinity units they
118 use.

119 In light of these ideas, we revisit the sea ice phase composition subject, by confronting
120 observations, theory (encapsulated in FREZCHEM) and frequently used computation
121 methods. We focus on three main diagnostics: brine salinity, the mass fraction of salt
122 that is hydrated into solid minerals, and liquid H₂O mass fraction. Our analysis suggests
123 that FREZCHEM is currently the most consistent source on sea ice phase composition,
124 and should therefore be used as a basis for revised sea ice phase composition. We also
125 propose a revised set of sea ice phase equations accounting for solid minerals. Finally,
126 we propose means to achieve compatibility with international standards, which requires
127 modification of TEOS-10 below -6°C and above $S = 120$ g/kg. The updated sea ice
128 phase equations and the TEOS-10 expansion provide a revised basis for sea ice thermo-
129 dynamics. We first introduce the observational and theoretical materials used (Section
130 2), describe our results (Section 3) and discuss them (Section 4). The proposed mod-
131 ification of TEOS-10 is presented as an Appendix.

132 **2 Theoretical framework and observational sources**

133 A complete characterization of the sea-ice composition is given by the mass frac-
134 tions of all of its constituents. Yet most applications need only a few diagnostics, in most
135 cases, brine salinity and liquid fraction. In this section, we define the main sea ice phase
136 composition diagnostics discussed in this paper, then review the observational and the-
137 oretical sources available to constrain them.

138 **2.1 Diagnostics of sea ice phase composition**

139 Our system is an isolated unit mass of H₂O and sea salt species with varying to-
 140 tal mass but fixed relative proportions of the different salts, as given by the standard sea-
 141 water composition (*Millero et al.*, 2008), at standard atmospheric pressure and thermo-
 142 dynamic equilibrium. The equilibrium assumption holds at time scales larger than a few
 143 minutes if only the ice-brine system is considered (*Griewank and Notz*, 2013). The equi-
 144 librium time scale can reach up to a few weeks if the slowest minerals such as gypsum
 145 are considered (*Marion et al.*, 1999). The system is either in the state of sea ice (if partly
 146 or entirely solid) or seawater (if entirely liquid). State variables are temperature T (ITS-
 147 90 °C, *Preston-Thomas*, 1990) and absolute bulk salinity S (g/kg, *Millero et al.*, 2008).
 148 The latter is defined as the absolute salinity of a well stirred, melted sea ice sample, of
 149 much larger size than individual brine inclusions. We seek to express phase composition
 150 diagnostics as functions of T and S .

151 Several extra assumptions are worth mentioning. Since we consider a unit mass as
 152 our fundamental system of interest (as done in FREZCHEM), most density-related is-
 153 sues can be discarded. In particular, we ignore gas bubbles as they have negligible mass.
 154 As phase relationships are derived in an isolated system framework, all heat and mass
 155 exchange (e.g. brine drainage) processes are ignored. Similarly, the textural type of sea
 156 ice (columnar or granular) is not considered. This is because textural types correspond
 157 to varying layouts of ice with the same Ih crystal structure, and therefore do not affect
 158 phase equilibrium. We also neglect pressure, the consequences of which are expectedly
 159 small but hard to evaluate in the present context of understanding.

160 At equilibrium, the chemical composition of brine (with regard to solutes) solely
 161 depends on T (*Feistel and Hagen*, 1998), hence brine salinity S_{br} is only function of T :
 162 brine inclusions are at their freezing point, which establishes a direct correspondence be-
 163 tween both. This relation $S_{br}(T)$, called the *liquidus curve* is the reciprocal of the re-
 164 lation between the seawater freezing point and salinity, $T_f(S)$. That brine salinity solely
 165 depends on temperature at thermal equilibrium has long been assumed in thermodynamic
 166 sea ice formulations (e.g. *Ono*, 1967; *Worster*, 1992; *Bitz and Lipscomb*, 1999).

167 A well-behaved liquidus curve should verify two constraints. First, fresh ice should
 168 have 0°C as a freezing point, hence S_{br} should be nil on $T = 0^\circ\text{C}$. Second, the liquidus
 169 curve should intersect the eutectic point. We set the eutectic temperature to $T_e = -36.2^\circ\text{C}$,

170 following the theoretical arguments of *Marion et al.* (1999), and considering the *Gitter-*
 171 *man* (1937) crystallization pathway as our reference. The eutectic salinity can hardly
 172 be determined experimentally: it corresponds to the salinity of brine with negligibly small
 173 volume, reached just above the eutectic temperature. Our choice for the eutectic salin-
 174 ity is to evaluate the third-order liquidus polynomial expression (regressed on selected
 175 observations and termed POLY3, see Section 2.3.1) on $T = T_e$, giving $S_e = 250.6146$ g/kg.

176 The mass fraction of salt hydrated into minerals ϕ_{sm}^{salt} is proportional to the total
 177 mass of salt in the system, hence to S . As each mineral is in equilibrium with brine, and
 178 the composition of brine depends on T only, we postulate that ϕ_{sm}^{salt} follows:

$$\phi_{sm}^{salt} = f_{sm}(T) \cdot S, \quad (1)$$

179 where f_{sm} , the mass fraction of total salt complexed into minerals is only a function of
 180 T . For $f_{sm} = 0$, there are no minerals in the system. For $f_{sm} = 1$, all salts are stored
 181 into minerals, which must be the case below the eutectic temperature. In their study fo-
 182 cused on mirabilite, *Butler et al.* (2016a, equation 6) make similar assumptions and reach
 183 a comparable but slightly different formulation of mirabilite mass fraction.

184 The mass fraction of brine (or liquid fraction ϕ_{br}) is another important diagnos-
 185 tic. Let us first write bulk salinity as the sum of brine and mineral contributions:

$$S = \phi_{br} \cdot S_{br}(T) + f_{sm}(T) \cdot S. \quad (2)$$

186 Rearranging terms, we get the liquid fraction:

$$\phi_{br}(S, T) = \left(1 - f_{sm}(T)\right) \cdot \frac{S}{S_{br}(T)}, \quad (3)$$

187 an expression close to that of *Assur* (1958). Classically used forms (e.g. *Bitz and Lip-*
 188 *scomb*, 1999; *Notz and Worster*, 2009) ignore minerals. The liquid fraction simplifies into
 189 $\phi_{br} = S/S_{br}(T)$, which is reasonable as long as the mass fraction of minerals is negli-
 190 gibly small, but does not attain zero at T_e and below.

191 In some instances, rather than liquid fraction, one needs to retrieve the mass frac-
 192 tion of liquid H_2O , noted $\phi_{br}^{H_2O}$. The latter is brine fraction less the dissolved salt frac-
 193 tion (which for brine salinity in g/kg is $\phi_{br} S_{br} \cdot 10^{-3}$). Hence $\phi_{br}^{H_2O}$ directly relates to
 194 brine fraction:

$$\phi_{br}^{H_2O}(S, T) = \phi_{br}(S, T) \cdot \left(1 - S_{br}(T) \cdot 10^{-3}\right). \quad (4)$$

195 Using equation (4), one can derive liquid H₂O mass fraction from T and S through liq-
 196 uid mass fraction and salinity. An alternative expression directly relating $\phi_l^{\text{H}_2\text{O}}$ to f_{sm}
 197 and S_{br} can be obtained by substituting (3) into (4).

198 Another frequently used quantity is brine volume fraction (ϕ_{br}^v). Mass and volume
 199 fractions are similar but quantitatively different. Following a similar development for solid
 200 fractions (*Notz, 2005, page 44*) liquid mass and volume fractions can be converted into
 201 each other:

$$\phi_{br} = [1 + (1/\phi_{br}^v - 1)\rho_i/\rho_{br}]^{-1}, \quad (5)$$

$$\phi_{br}^v = [1 + (1/\phi_{br} - 1)\rho_{br}/\rho_i]^{-1}, \quad (6)$$

202 where ρ_i and ρ_{br} refer to pure ice and brine densities, for which following *Cox and Weeks*
 203 (*1983*), we used and the expressions of *Pounder (1965)* and *Zubov (1945)*. In the upcom-
 204 ing sections, we will evaluate what theory and observations tell us about f_{sm} , S_{br} and
 205 ϕ_{br} .

206 **2.2 Sea ice phase relationships from the Gibbs-Pitzer theory (FREZCHEM).**

207 The Gibbs-Pitzer approach (*Pitzer, 1991*) implemented in the FREZCHEM code
 208 (*Marion et al., 2010*), provides practical means to calculate the theoretical equilibrium
 209 composition of partly frozen electrolyte solutions – of which our system is a particular
 210 example. FREZCHEM is widely used to explore cold geochemical processes in the Earth’s
 211 polar regions, and to explore life limits on Europa and Mars. Mass conservation at tem-
 212 perature T and salinity S , split over the different phases and integrated over the differ-
 213 ent chemical species considered by FREZCHEM is given by:

$$1 = \phi_{br}^{\text{H}_2\text{O}} + \phi_{br}^{\text{salt}} + \phi_{ice}^{\text{H}_2\text{O}} + \phi_{sm}^{\text{H}_2\text{O}} + \phi_{sm}^{\text{salt}}. \quad (7)$$

214 The different terms refer to mass fractions (ϕ 's) of liquid H₂O, dissolved salts, pure ice
 215 (solid H₂O) and solid minerals split into H₂O and salt contributions, all being expressed
 216 per unit mass of sea ice. The phase diagram shown in Figure 1, drawn from post-processed
 217 FREZCHEM outputs with $S = 5$ g/kg (typical of first-year winter sea ice, taken for
 218 illustration) shows the distribution of mass among the different phases of the system, from
 219 the eutectic to the freezing temperature.

220 The principle of the Gibbs-Pitzer approach is to minimize the Gibbs free energy,
 221 in a form accounting for binary and ternary ion interactions, described through *Pitzer*

222 parameters fitted on experimental data. FREZCHEM includes tabulations of *Pitzer* pa-
 223 rameters and a minimization algorithm for the Gibbs free energy. Based on a specified
 224 reference composition for an aqueous solution at a reference temperature, FREZCHEM
 225 gives the solute and mineral composition (activity coefficients and molal concentrations)
 226 at any temperature down to the eutectic limit. Because FREZCHEM is an equilibrium
 227 model, it is consistent with the *Gitterman* crystallization pathway (obtained from long
 228 equilibration times) with a eutectic temperature at -36.2°C (*Marion et al.*, 1999).

229 To derive the detailed Gibbs-Pitzer sea ice phase diagram, we used FREZCHEM
 230 13.3, configured to simulate the cooling and progressive freezing of $M = 1000 + M_s$
 231 grams of standard seawater, made of 1000 g of H_2O and $M_s = 1000 \cdot S/(1000 - S)$
 232 grams of salt, adequately distributed among the 15 species of standard seawater (*Millero*
 233 *et al.*, 2008, Table 4). Following the composition of standard seawater, we also imposed
 234 385 ppm of CO_2 and $\text{pH} = 8.1$. FREZCHEM was run 41 times for $S = 0.3, 1, 2, \dots, 40$
 235 g/kg. The cooling started from $T = 0^{\circ}\text{C}$ down to the eutectic temperature over -0.1°C
 236 steps. Minerals precipitated at temperatures independent of S (Table 1) and the sim-
 237 ulated sequence nearly matches that found by *Butler et al.* (2016a). Differences in tem-
 238 peratures of precipitation are typically within 0.1°C and could be due to slightly differ-
 239 ent model version, input files or to numerical precision.

240 To derive mass fractions, the following FREZCHEM outputs were retained for post-
 241 processing: the mass of ice Ih (g), the mass of liquid H_2O (g), the molality of the 21 con-
 242 sidered solutes (mol/kg liquid H_2O), and the moles of each of the considered 101 min-
 243 erals (mol/kg), of which only 8 were found in detectable amounts (Table 1). All these
 244 outputs were stored over the 363×41 T - S grid for further processing. Throughout pro-
 245 cessing, we used the *Wieser* (2006) table of atomic weights to compute molar masses of
 246 individual ions, solutes and minerals, as recommended by *Millero et al.* (2008).

247 Let us now describe how S_{br} , f_{sm} , ϕ_{br} and $\phi_{br}^{\text{H}_2\text{O}}$ were derived. For each solute, the
 248 mass fraction $C_i(S, T)$ (g/kg brine) was retrieved from molality. The FREZCHEM brine
 249 salinity value is the sum of the C_i 's over all solutes:

$$S_{br}^{\text{FZC}} = \sum_{\text{solute}} C_i. \quad (8)$$

250 For each mineral, the mass fractions of solid salt $\phi_{sm,i}^{salt}$ (per unit mass of the system, g/kg)
 251 were derived as well. The salt fraction in minerals could be diagnosed as

$$f_{sm}^{FZC} = \frac{1}{S} \cdot \sum_{\text{minerals}} \phi_{sm,i}^{salt}. \quad (9)$$

252 A check indicated that the FREZCHEM C , S_{br} and f_{sm} values are as expected indepen-
 253 dent of S . The liquid H₂O fraction was diagnosed by dividing the mass of liquid H₂O
 254 by M . Brine mass fraction ϕ_{br} was finally retrieved from Equation 4.

255 To expand f_{sm}^{FZC} and S_{br}^{FZC} within the 363 discrete temperature values, we apply
 256 piecewise cubic hermite interpolation. To expand $\phi_{br}^{H_2O}$ we apply similar cubic interpo-
 257 lation in T and, because $\phi_{br}^{H_2O}$ is linear in S , we used linear interpolation in S .

258 2.3 Observational sources

259 Now we turn to the observational sources that constrain the sea ice phase compo-
 260 sition. We strived to retain observational sources only. We focused on directly measured
 261 quantities in order to avoid inconsistencies due to processing.

262 2.3.1 Liquidus and freezing temperature

263 We retained four sources documenting either the liquidus salinity as a function of
 264 temperature or equivalently the freezing point of seawater versus salinity (*Gitterman*,
 265 1937; *Nelson and Thompson*, 1954; *Doherty and Kester*, 1974; *Butler et al.*, 2016b, see
 266 Table 2, Figure 2). Unlike previous authors, we did not retain the model calculations of
 267 *Assur* (1958), as they were computational derivations of the *Nelson and Thompson* (1954)
 268 observations. All retained studies reported absolute salinities in g/kg. The conversion
 269 from ITP-68 to ITS-90 temperature scale was applied to the observations prior to 1990
 270 (*Gitterman*, 1937; *Nelson and Thompson*, 1954; *Doherty and Kester*, 1974).

271 The experimental contexts in which these observations were acquired differ in a num-
 272 ber of ways, in particular regarding the apparatus, instruments and type of seawater used,
 273 protocols and equilibration times. They therefore have varying T - S precision and range.
 274 We attempted to summarize these differences in Table 2, and discuss the most impor-
 275 tant points hereafter.

276 The experiments of *Gitterman* (1937) and *Nelson and Thompson* (1954) aimed to
 277 describe the sequence of precipitating salts from the freezing of seawater. To that pur-

278 pose, they followed the composition of the liquid phase in frozen artificial and natural
 279 seawater samples, respectively, at different temperatures. We used tabulated values pro-
 280 vided in these two studies. *Gitterman* (1937) directly provides absolute salinity read-
 281 ings (their Table 7). *Nelson and Thompson* (1954) provide mass concentration for the
 282 most important ions (Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Cl^- , SO_4^{2-} , their Table 1). To get absolute
 283 salinity, we summed these, excluding samples without SO_4^{2-} reported value, which would
 284 under-estimate salinity by up to about 5-10%. Despite both studies being characterized
 285 by different incubation times (up to 4 weeks for *Gitterman* and a few hours for *Nelson*
 286 *and Thompson*) and crystallization pathways (*Marion et al.*, 1999), there is no clearly
 287 detectable liquidus salinity difference between both studies.

288 The observations of *Doherty and Kester* (1974) are high-precision measurements
 289 of the freezing point of seawater over the observed seawater salinity range. These data
 290 were indirectly used for the elaboration of TEOS-10 (see Section 6.3 of *Feistel*, 2008).
 291 They are provided in two tables in the original publication. We followed *Feistel* (2008)
 292 and corrected for the effect of air saturation and converted from IPTS-68 to ITS-90 tem-
 293 perature scales, even though such conversions appear negligible for our purposes.

294 *Butler et al.* (2016b) focussed on the precipitation of mirabilite in synthetic Sim-
 295 plified seawater samples (*DOE*, 1994) using close-bottle incubation methods and an av-
 296 erage incubation time of 53 days, using the opportunity to note the freezing point of sea-
 297 water, down to -20.6°C . Synthetic Simplified seawater only has the 6 major ions, in slightly
 298 higher proportions than in natural seawater, in order to compensate for the missing mi-
 299 nor ions while preserving salinity.

300 In conformity with our assumption that the *Gitterman* (1937) crystallization path-
 301 way holds, all of our analyses are restricted to the $[-36.2, 0^\circ\text{C}]$ temperature range. Al-
 302 together, we retained 64 T - S couples covering the $[-35.49, -0.37^\circ\text{C}]$ temperature and
 303 $[6.97, 248.4 \text{ g/kg}]$ salinity ranges (symbols in Fig. 2). Between -20 and -10°C , where
 304 data coverage is the largest, we note a typical uncertainty of about 2.5 g/kg for S_{br} , which
 305 corresponds to a temperature uncertainty of $\sim 0.15^\circ\text{C}$, that can be attributed to vary-
 306 ing apparatus, incubation time and type of samples used.

307 A 3rd order polynomial was fitted on the selected 64 observations under the con-
 308 straint that $S_{br} = 0$ at $T = 0$:

$$S_{br}^{POLY3} = -18.7 T - 0.519 T^2 - 0.00535 T^3. \quad (10)$$

309 This fit (black line in Fig. 2) referred to as POLY3 was used to provide the best obser-
 310 vational estimate of the eutectic salinity $S_e = 250.6146$ g/kg.

311 **2.3.2 Minerals**

312 There are also a few observational sources that can help to construct the solid salt
 313 fraction function f_{sm} . Among the visual (e.g., *Light et al.*, 2009; *Geilfus et al.*, 2013),
 314 analytical (e.g., *Gitterman*, 1937; *Butler et al.*, 2016a) and X-ray methods (*Butler and*
 315 *Kennedy*, 2015) that have been applied, we retain analytical estimates of mirabilite mass
 316 per unit mass of sea ice by *Butler et al.* (2016a) using the fit they provide (their Table
 317 4). For reference, we also converted the tabulated salt mass of minerals from the calcu-
 318 lations of (*Assur*, 1958, Table 3) into f_{sm} .

319 **2.3.3 Liquid H₂O fraction**

320 Liquid fraction cannot be directly measured, but liquid H₂O can be retrieved by
 321 Nuclear Magnetic Resonance (NMR) (*Richardson and Keller*, 1966). The NMR signal,
 322 namely the area under the NMR absorption curve, is related to the liquid H₂O mass frac-
 323 tion in a sample. *Richardson and Keller* (1966) measured the NMR absorption curves
 324 from frozen seawater samples at 10.022 and 35.035 g/kg, from freezing temperatures down
 325 to -50°C . Since these experiments span a wide region of the T - S space and are well doc-
 326 umented, they are suitable for an evaluation of liquid water fraction. Their table data
 327 included some unreproducible processing, hence we chose to digitize the raw NMR liq-
 328 uid H₂O mass fraction estimates presented in their Figure 2 and 3. We specifically use
 329 the ratio between NMR area at temperature T to NMR area at 0°C , where the sample
 330 is all liquid (termed Q_T/Q_0 in their paper). The authors mention that their results were
 331 reproducible within 1% accuracy, to which must be added the digitizing uncertainty.

332 **2.4 The liquidus curve from a modified TEOS-10**

333 Another source to be considered is the International Thermodynamic Equation Of
 334 Seawater, aka *TEOS-10* (*IOC, SCOR and IAPSO*, 2010), which provides means to con-
 335 sistently derive all seawater's thermodynamic properties, including the freezing point of
 336 seawater. The freezing point can be numerically inverted – resulting into a liquidus curve.
 337 TEOS-10 is now the international reference used in the framework of oceanographic anal-

338 yses. It is also implemented into some ocean models and thermodynamic sea ice formu-
 339 lations should ideally be consistent with TEOS-10.

340 The information on the seawater freezing point that was blended into the TEOS-
 341 10 seawater Gibbs function comes from FREZCHEM (*Feistel, 2008*), found to agree within
 342 a few mK with the observations of *Doherty and Kester (1974)*. Operationally, the TEOS-
 343 10 freezing point derives from the freezing condition equation, stating the equality of the
 344 chemical potentials of ice and of water in seawater.

345 The first initial obstacle towards a TEOS-10 liquidus curve is that the TEOS-10
 346 validity range is limited to $S < 120$ g/kg, which is insufficient to get a liquidus curve
 347 over the proper salinity range. One obvious initial attempt to resolve that issue is to re-
 348 lieve the 120 g/kg salinity barrier from the TEOS-10 computations, that is, continue to
 349 use the seawater Gibbs function of TEOS-10 outside its range of validity. The resulting
 350 freezing point (dashed blue curve in Figure 2) is not only imprecise as expected, it is also
 351 not monotonic, reaching a maximum of -22.3°C near $S = 330$ g/kg, hence the recip-
 352 rocal function (the liquidus curve) can only be defined above -22.3°C .

353 The reference TEOS-10 is therefore inappropriate for the estimation of a proper
 354 liquidus curve. It is however possible to add a small modification to TEOS-10 to address
 355 this problem, which we detail in Appendix A and only summarize here. In this devel-
 356 opment, as explained by *Feistel and Hagen (1998)*, brine is viewed as the continuation
 357 of seawater, being characterized by the same Gibbs function, expressed as a function of
 358 brine salinity. This approach is well posed: above the freezing point, brine fraction is 1
 359 and bulk and brine salinity coincide.

360 Turning now to the desired correction to the TEOS-10 Gibbs potential, the ba-
 361 sic idea is to introduce a perturbation $g^c(S)$ to the TEOS-10 seawater Gibbs potential
 362 $g^{TEOS-10}$:

$$g(S_{br}, T) = g^{TEOS-10}(S_{br}, T) + g^c(S_{br}). \quad (11)$$

363 g^c should be constructed so as to minimize changes in g within the TEOS-10 salinity range,
 364 and to fit the freezing temperature at higher salinities (see Fig. A2). The most conve-
 365 nient form we found for the perturbation function is:

$$g^c(S_{br}) = \begin{cases} 0 & \text{if } S_{br} < S_0 = 120 \text{ g/kg,} \\ a \cdot (S_{br} - S_0)^4 & \text{otherwise (where } a = 1.2370 \times 10^{-5} \text{ J/g}^4 \cdot \text{kg}^3\text{),} \end{cases} \quad (12)$$

366 which has the few desired properties. The liquidus curve derived from the modified Gibbs
 367 function (mTEOS-10, solid blue curve in Figure 2) is now reasonably precise down to
 368 T_e . It also preserves TEOS-10 integrity below $S_0 = 120$ g/kg and ensures the continu-
 369 ity of the Gibbs function's derivatives up to order 4. Finally, it is eutectic compliant by
 370 definition. The method outlined above and developed in the appendix is efficient to de-
 371 rive a proper liquidus curve from the seawater Gibbs function. However, there could be
 372 extra deviations to the Gibbs function off the freezing curve that cannot be inferred from
 373 our method.

374 **3 Results**

375 In this section, we describe how the Gibbs-Pitzer theory (FREZCHEM), observa-
 376 tions and classical computation methods compare in terms of liquidus curve, salt frac-
 377 tion in minerals and liquid fraction.

378 **3.1 Liquidus curve**

379 The liquidus curves from the various retained sources are presented graphically, ver-
 380 sus temperature (Figure 2). The computation methods (empirical functions, TEOS-10)
 381 that were used are listed in Table 3. For quantitative comparison, the 64 retained ob-
 382 served temperatures of Section 2.3 were used as a basis for the liquidus salinity compu-
 383 tation. The mean statistics of the comparison between the calculated salinities with ob-
 384 served values are given in Table 4.

385 All sources give the increase in brine salinity with decreasing temperature, and most
 386 of them predict a monotonic increase from 0 to ~ 250 g/kg with an initially rapid in-
 387 crease near the freezing temperature, then slowing down approaching T_e .

388 The FREZCHEM liquidus provides the best match with observational values, giv-
 389 ing a slightly positive bias (1.1 g/kg), a root-mean-square (RMSE) error of 1.9 g/kg and
 390 a standard deviation of error (STDE) of 2.5 g/kg, characterizing the current levels of un-
 391 certainty on the liquidus salinity. Uncertainties increase with decreasing temperature:
 392 for instance, the FREZCHEM-obs RMSE is more than three times smaller over the TEOS-
 393 10 validity range (RMSE= 0.5 g/kg, STDE = 1.15 g/kg) than over the entire temper-
 394 ature range. Near-freezing temperatures are also where we have the most precise obser-
 395 vations (*Doherty and Kester, 1974*, hereafter DK74), as illustrated by the error versus

396 temperature plot (Fig. 2b). The precision of the DK74 observations clearly outcompetes
 397 the other observations, among which the observations of *Butler et al.* (2016b) seem the
 398 least biased compared to FREZCHEM.

399 FREZCHEM relies on a precise and coherent representation of thermo-chemical
 400 processes, which explains why it is able to capture the inflection in brine salinity at -22.9°C
 401 associated with the precipitation of hydrohalite. This constitutes a clear advantage of
 402 FREZCHEM over other approaches. For instance, the observation-based 3^{rd} order least-
 403 square fit (POLY3, black line in Fig. 2) cannot capture the liquidus inflection and does
 404 not reproduce observations as well as FREZCHEM (RMSE=2.3 g/kg, STDE = 3.2 g/kg).

405 Several other classically used approaches for estimation of the liquidus curve were
 406 also included in our evaluation (see Table 3). The simplest possible approach is to as-
 407 sume that the relation between T and S_{br} is linear (*Assur*, 1958). Such a relation would
 408 hold if brine was an ideal solution, i.e., if the different molecules that compose brine in-
 409 teracted all in the same way. This is seemingly valid until about -5°C , below which non-
 410 linearities become significant (see red dotted line in Fig. 2), leading to largely over-estimated
 411 brine salinities (> 100 g/kg) at low temperatures. The linear approach is used in the
 412 many sea ice models following the *Bitz and Lipscomb* (1999) thermodynamic formula-
 413 tion, based on the plausibly negligible impact of brine salinity errors on the energetics
 414 of the system (*Notz*, 2005).

415 Biogeochemical sea ice modules are sensitive to the large brine salinity bias at low
 416 temperature in the linear approach, notably for primary production (*Vancoppenolle and*
 417 *Tedesco*, 2017) and carbonate chemistry computations (*Moreau et al.*, 2015), calling for
 418 better brine salinity estimates. As an example of the many 3^{rd} order fits available, we
 419 retained the third-order polynomial of *Notz and Worster* (2009, NW09 in Table 3), fit-
 420 ted on the liquidus reconstruction of *Assur* (1958) over the $[-22.9, 0^{\circ}\text{C}]$ range. The NW09
 421 fit fullfills the fresh ice constraint, but not the eutectic constraint and expectedly spreads
 422 from observations below the hydrohalite precipitation point (solid red line in Fig. 2).

423 The last empirical approach included in our evaluation is the *Cox and Weeks* (1986,
 424 their Table 2) relationship (gray line in Fig. 2, CW86 in Table 3), widely used in the ob-
 425 servational literature. CW86 combines three 3^{rd} order polynomials regressed on *Assur*
 426 (1958) data and holds from -2 to -54°C (the eutectic temperature under the *Nelson*
 427 *and Thompson* crystallization pathway). Because it does not cover the high tempera-

428 ture range, the CW86 approach is unsuitable for modelling. Yet the CW86 function still
 429 provides precise liquidus estimates (RMSE = 2.9 g/kg, STDE= 3.5 g/kg), including the
 430 -22.9°C discontinuity, among the most precise estimates retained.

431 The modified TEOS-10 (mTEOS-10) liquidus is in line with the best available es-
 432 timates. It is slightly less precise on average than other approaches (RMSE = 3.0 g/kg,
 433 STDE = 4.6 g/kg). It is remarkable that mTEOS-10 is the most precise estimation ap-
 434 proach over the TEOS-10 validity range, nearly as precise as FREZCHEM (RMSE =
 435 0.6 g/kg, STDE = 1.14 g/kg). In the $[-10, -20^{\circ}\text{C}]$ range, mTEOS-10 overestimates the
 436 liquidus salinity by about 5 g/kg and significantly underestimates it near the hydrohalite
 437 precipitation discontinuity (Fig 2e).

438 3.2 Minerals

439 Experimental sources for estimating the salt fraction in minerals f_{sm} are only a few
 440 (see Section 2.3). Figure 3 graphically depicts $f_{sm}(T)$ from FREZCHEM (grey line), the
 441 *Assur* (1958) computations (red dashed line), and the observation-derived fit of *Butler*
 442 *et al.* (2016a, hereafter B16a, blue squares), which only includes mirabilite and hence is
 443 valid until -22.9°C . Because mirabilite dominates by far the total mass of minerals above
 444 that temperature threshold, the B16b fit is in excellent agreement with FREZCHEM,
 445 which itself includes all minerals.

446 At -22.9°C , the fraction of salt in minerals consistently reaches about 10% accord-
 447 ing to all sources. Below -22.9°C , the only independent source available is *Assur* (1958).
 448 We find agreement with FREZCHEM within 10% until about -33°C , where f_{sm} becomes
 449 slightly less than 0.8, because both approaches converge on the precipitation of hydro-
 450 halite. We do not expect the solution of Pitzer equations given by FREZCHEM and the
 451 calculations of *Assur* to be exactly consistent, because of the many differences between
 452 them.

453 The last two jumps in f_{sm} predicted by FREZCHEM are mostly due to the pre-
 454 cipitation of meridianite and sylvite near -33.3°C and to magnesium chloride dodecahy-
 455 drate at -36.2°C (Table 1). The FREZCHEM crystallization sequence we get is close
 456 to but slightly different from similar FREZCHEM computations (*Marion et al.*, 1999;
 457 *Butler et al.*, 2016a). It is beyond the scope of this work to track down the origin of the

458 differences, but they are presumably due to protocol differences (FREZCHEM version,
459 specification of the input seawater composition).

460 3.3 Liquid H₂O fraction

461 Liquid mass (ϕ_{br}) or volume (ϕ_{br}^v) fractions are frequently used in sea ice studies,
462 but not directly observable. However what can be learned from liquid H₂O fraction ($\phi_{br}^{\text{H}_2\text{O}}$),
463 measurable by NMR, is in practice relevant to ϕ_{br} and ϕ_{br}^v . Indeed, these three quan-
464 tities are closely related to each other. This is illustrated in the two scatter plots of Fig-
465 ure 4, based on the FREZCHEM diagnostics over the entire T - S space. First, both $\phi_{br}^{\text{H}_2\text{O}}$
466 and ϕ_{br}^v are tightly linearly correlated with ϕ_{br} – the associated linear regression coef-
467 ficient is in both cases slightly smaller than 1. Second, the relation between $\phi_{br}^{\text{H}_2\text{O}}$, ϕ_{br}^v
468 and ϕ_{br} is strictly monotonic. $\phi_{br}^{\text{H}_2\text{O}}$ and ϕ_{br}^v prove systematically lower than liquid mass
469 fraction, with differences typically within 20 %. For liquid H₂O this is simply because
470 next to H₂O brine also contains dissolved salt. For brine volume fraction this is due to
471 the higher density of brine than that of the surrounding ice. Since ϕ_{br} and ϕ_{br}^v are nearly
472 equivalent to $\phi_{br}^{\text{H}_2\text{O}}$, the coming paragraphs are nearly entirely focused on the latter.

473 The liquid H₂O fractions from the various retained sources are presented graph-
474 ically, in an attempt to reproduce the two *Richardson and Keller* (1966) series of NMR
475 scans, run at two different salinities (10.022 and 35.035 g/kg) over the $[-35, 0^\circ\text{C}]$ tem-
476 perature range (Figure 5). For a quantitative evaluation of T - and S -based computations
477 of the liquid water fraction, the observed T and S were used to estimate the observed
478 liquid water fraction, for several variants in the details of the computations. In all cases
479 but two, calculations were based on equations (3) and (4), which require intermediate
480 calculations of liquidus salinity and solid salt fraction, for which several choices were tested.
481 The mean statistics of the comparison with the 20 retained observational data points (Sec-
482 tion 2.3.3) are given in Table 5.

483 All observational and theoretical sources suggest a decrease in $\phi_{br}^{\text{H}_2\text{O}}$, from nearly
484 $1 - S \times 10^{-3}$ at the freezing temperature to nearly 0 at the eutectic temperature, and
485 all sources obviously capture the increase in $\phi_{br}^{\text{H}_2\text{O}}$ with bulk salinity. Both FREZCHEM
486 and observations feature discontinuities. Observations indicate a single discontinuity at
487 -22.9°C , the temperature of hydrohalite precipitation. There are three discontinuities
488 in FREZCHEM, each of them being associated with the precipitation of a mineral. The

489 absence of the last two discontinuities from observations is not surprising as (i) these are
 490 characteristic of the *Gitterman* equilibrium crystallization pathway simulated by FREZCHEM
 491 and (ii) the equilibration time is not mentioned in their study, it is unlikely that the
 492 required weeks for equilibration of samples (*Marion et al.*, 1999) were actually respected
 493 by *Richardson and Keller* (1966).

494 FREZCHEM (grey circles in Fig 5) provides the most consistent $\phi_{br}^{\text{H}_2\text{O}}$ estimate with
 495 observations and is slightly biased (1.1 g/kg, RMSE = 8.6 g/kg, STDE = 13.3 g/kg), quan-
 496 tifying the current uncertainty levels on the liquid H₂O fraction. Uncertainties seem in-
 497 dependent of temperature, but they increase from a RMSE = 2.9 g/kg for $S = 10.022$
 498 g/kg, to 10.1 g/kg for $S = 35.035$ g/kg – provided we rule out the one sample processed
 499 at the highest temperature (see Fig. 5b).

500 Let us now discuss the few other simpler calculation techniques for liquid water frac-
 501 tion. Computations stem from equations (3) and (4) with prescribed functional depen-
 502 dencies for $S_{br}(T)$ and $f_{sm}(T)$. Using interpolated FREZCHEM values for S_{br} and f_{sm}
 503 gives virtually the same $\phi_{br}^{\text{H}_2\text{O}}$ error statistics as for the direct FREZCHEM diagnostic,
 504 which confirms the internal consistency of the equations. The small difference is likely
 505 due to numerical precision or interpolation errors. Keeping the FREZCHEM values for
 506 f_{sm} but now using the slightly less precise liquidus estimates (mTEOS-10, blue curve
 507 in Fig. 5; POLY3, not shown but similar) instead of the FREZCHEM function only slightly
 508 deteriorates the liquid water error statistics (RMSE = 8.9 g/kg, STDE = 13.5 g/kg).

509 Accounting for minerals is necessary to reproduce the discontinuities in liquid con-
 510 tent. Once f_{sm} is set to zero (i.e., once minerals are neglected, as classically done in sea
 511 ice models) the hydrohalite discontinuity at -22.9°C is lost, and errors in liquid H₂O
 512 fraction increase toward lower temperatures. With no minerals and a non-linear liquidus
 513 (black curve in Fig. 5), $\phi_{br}^{\text{H}_2\text{O}}$ is overestimated, in particular below the hydrohalite dis-
 514 continuity. With no minerals and linear liquidus (red dashed curve in Fig. 5), $\phi_{br}^{\text{H}_2\text{O}}$ is
 515 underestimated for most of the temperature range.

516 The widely used empirical formulation for brine volume fraction of *Cox and Weeks*
 517 (1983, hereafter CW83) – a non-linear, piece-wise combination of 3^{rd} order functions –
 518 was also included in the analysis. The CW83 volume fraction was first converted into
 519 mass fraction from equation (5), using the CW83 expressions suggested for ice and brine
 520 densities. Then the result was combined with the liquidus salinity of *Cox and Weeks* (1986)

521 and converted into liquid H₂O fraction using equation (4), see Table 5. The result is slightly
 522 less consistent with observations than FREZCHEM (RMSE = 10.5 g/kg, STDE = 12.4
 523 g/kg) over its claimed validity range ($[-30, -2^{\circ}\text{C}]$).

524 We now finally turn to brine mass fraction estimates, taking FREZCHEM as a ref-
 525 erence in the absence of observational values (Figure 6, Table S1). All findings on $\phi_{br}^{\text{H}_2\text{O}}$
 526 practically apply to ϕ_{br} . The differences in calculated brine fraction and FREZCHEM
 527 values over the entire T - S space generalize Figure 5. With minerals included, FREZCHEM
 528 and mTEOS-10 agree within 3 g/kg in terms of brine fraction. Neglecting minerals in-
 529 duces the largest brine fraction errors, of up to about 20-30 g/kg in the low tempera-
 530 ture range. Uncertainties at typical T - S values are generally low.

531 4 Discussion and conclusions

532 We revisited the thermodynamics of sea ice phase composition by confronting ob-
 533 servations, theory and classical computation methods, from a revised formulation of the
 534 problem and a thorough account for available sources of information. We focused on two
 535 important diagnostics: brine salinity and liquid H₂O fraction (a close proxy of brine mass
 536 or volume fraction). All materials presented here are based on ITS-90 Celsius temper-
 537 atures (*Preston-Thomas*, 1990) and absolute salinities in g/kg (*Millero et al.*, 2008), which
 538 is a prerequisite for compatibility with TEOS-10.

539 Observations of brine salinity and liquid H₂O fraction were carefully selected from
 540 a literature survey. As a theoretical reference, we used a detailed description of sea ice
 541 phase composition derived from FREZCHEM, a numerical code applying the Gibbs-Pitzer
 542 theory to aqueous solutions and widely used in Earth and Planetary science (*Marion et al.*,
 543 2010). The considered T - S range encompasses virtually all sea ice conditions encoun-
 544 tered on Earth: bulk salinity ranges over [0.3, 40 g/kg] and temperature goes from eu-
 545 tectic to liquid seawater conditions $[-36.2, 0^{\circ}\text{C}]$. Standard seawater composition (*Millero*
 546 *et al.*, 2008) was strictly imposed at 0°C . Brine salinity, liquid H₂O fraction and brine
 547 mass fraction were derived based on FREZCHEM outputs, among other phase compo-
 548 sition diagnostics.

549 The agreement between observations and the Gibbs-Pitzer theory (FREZCHEM)
 550 is remarkable: among all tested methods, FREZCHEM is the most faithful to observa-
 551 tions, both in terms of brine salinity and liquid H₂O mass fraction. The agreement is

552 impressive given how independent FREZCHEM and the selected observations are, rais-
 553 ing confidence in both. The resulting view of the sea ice phase composition does not sig-
 554 nificantly depart from the standard one (*Assur, 1958; Petrich and Eicken, 2009*): sea
 555 ice is typically ice and brine above -22.9°C with a small fraction of mirabilite, taking
 556 up to 10% of the salt mass. Most mineral precipitation occurs in the form of hydrohalite
 557 between -22.9°C and the eutectic temperature (-36.2°C) (Figure 1). The most notable
 558 change in the revised phase diagram is a different succession of precipitating minerals,
 559 and a eutectic temperature at -36.2°C and not -54°C , consistently with the long equi-
 560 libration times in the *Gitterman* crystallization pathway.

561 Uncertainties in sea ice phase composition are now better understood and quan-
 562 tified. First, the typical error (RMSE) in brine salinity is 1.9 g/kg, larger near the hy-
 563 drohalite precipitation temperature and smallest near the freezing point. Second, the mean
 564 uncertainty in liquid mass fraction of H_2O , was evaluated at 8.6 g/kg (corresponding to
 565 0.8% in the usual units, namely % of mass). Errors in brine mass or volume fractions
 566 should have similar magnitude. Below -22.9°C , we find generally larger uncertainties
 567 in liquid fraction, because of unresolved ambiguities in the mineral precipitation sequence.

568 Among all the assumptions made, neglecting pressure has the least known conse-
 569 quences. Ignoring pressure effects on the freezing point is reasonable at the ocean sur-
 570 face. Pressure effects might be comparatively larger within brine inclusions, and this topic
 571 just starts being studied. Calculations based on isolated brine pocket volume changes
 572 (*Crabeck et al., 2019*) suggest typical pressures of 10 bars, and values up to 75 bars. To
 573 envision possible implications on sea ice phase composition, we ran FREZCHEM at $p =$
 574 100 bars. Even at such pressures, changes in brine salinity and in the predicted sequence
 575 of precipitating minerals, relative to runs at 1 bar, were minor. Another instance of pos-
 576 sibly significant pressure-related effects is marine ice, formed under marine ice shelves
 577 from the freezing of seawater, several hundreds of meters deep into seawater, where the
 578 seawater freezing point is a few tenths of K lower than at the surface. Admittedly, in Earth
 579 System Models, the absence of pressure as a state variable in our proposed sea ice phase
 580 relationships could be a source of inconsistency between the ice and seawater thermo-
 581 dynamic formulations, at depth, and provided that marine ice is treated as sea ice. How-
 582 ever, current understanding suggests that marine ice often proves nearly fresh (*Eicken*
 583 *et al., 1994*). More generally, how marine ice thermodynamics should be represented in
 584 models is open to question.

585 There are also ambiguities in the sequence of crystallizing minerals that remain un-
586 resolved. This is notably because all formulations to date assume thermal equilibrium.
587 In natural sea ice, temperature can change over a few hours, whereas the kinetics of mirabilite
588 dissolution and gypsum precipitation are slower, slow enough to require sample equili-
589 bration times of up to a few weeks in the *Gitterman* equilibrium crystallization path-
590 way (*Marion et al.*, 1999).

591 Another source of uncertainty is deviation from standard seawater composition. Com-
592 positional differences due to source seawater composition are expectedly minor (*McDougall*
593 *et al.*, 2012). Mineral precipitation, could also change the composition of brine with re-
594 spect to seawater. Hence brine convection (*Wells et al.*, 2011) exchanging brine and sea-
595 water could to some extent modify the sea ice composition. Yet, as brine convection and
596 mineral precipitation are most efficient at fairly different depths in the ice, the former
597 near the ice base, the latter near the ice surface, such deviations in brine composition
598 seem unlikely to play a large role. By all means, to resolve these issues, one should re-
599 lieve the phase equilibrium hypothesis and include the kinetics of mineral precipitation,
600 which would bring the model’s complexity to a much higher level. Since errors in brine
601 composition remain relatively low (*Marion et al.*, 1999), we argue that these uncertain-
602 ties are of minor importance as far as a salt budget is concerned and that there is no ur-
603 gent need for such modifications.

604 We now turn to a few recommendations on working practises for calculating brine
605 salinity and mass fraction in the context of observational measurements. Depending on
606 the precision required, different computation approaches to the sea ice phase composi-
607 tion diagnostics can be adopted. The most precise and consistent source available for
608 such computations is FREZCHEM. Since running it can take time, we provide the nu-
609 merical FREZCHEM full phase composition description in netcdf format as supplemen-
610 tary material, which can readily be used. The classical fits of *Cox and Weeks* (1983, 1986)
611 are very good but slightly less precise approximations, and are more limited in cover-
612 age. For temperatures above -22.9°C , using the POLY3 fit (eq. 10) to compute brine
613 salinity and neglecting minerals to compute brine fraction is simple and precise enough
614 for most purposes. The modified TEOS-10 Gibbs function – keeping TEOS-10 unchanged
615 over its validity range and giving a liquidus curve in much better agreement with obser-
616 vations down to the eutectic temperature – is most useful for modelling purposes.

617 The revised framework proposed in Section 2 could make sea ice models more pre-
618 cise with respect to phase composition, improve their physical robustness, notably by
619 considering the presence of minerals, and bring possible consistency with TEOS-10. Yet
620 doing so would require in-depth modifications of the thermodynamic core of existing mod-
621 els and increase their complexity. Whether that would be worth systematic implemen-
622 tation requires investigation. It already seems clear that since sea ice process models in-
623 cluding biogeochemistry are quite sensitive to brine salinity errors (*Moreau et al.*, 2015;
624 *Vancoppenolle and Tedesco*, 2017) they would benefit from using at least the POLY3 fit
625 presented here. Coupled ice-ocean models would also gain from TEOS-10 consistency
626 within ocean and sea ice components. Major impacts on large-scale sea ice dynamics are
627 not expected, but the additional physical realism and consistency would reduce uncer-
628 tainties in the simulated thermodynamics.

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Table 1. Precipitating minerals in FREZCHEM 13.3, along with their highest temperature of occurrence and their mass fraction of total salt f_{sm} at the eutectic temperature ($T_e = -36.2^\circ\text{C}$). $f_{sm}(T_e)$ is expressed as the mass of non-H₂O species within the considered mineral divided by the total mass of sea salt in the considered unit mass. FREZCHEM was run with standard seawater (Millero *et al.*, 2008), from 0°C down to -36.2°C , using 0.1°C steps.

Mineral	Formula	T ($^\circ\text{C}$)	$f_{sm}(T_e)$ (%)
Ikaite	$\text{CaCO}_3 \cdot 6 \text{H}_2\text{O}$	-4.9	0.2
Gypsum	$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$	-6.2	3.6
Mirabilite*	$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	-6.4	0
Hydrohalite	$\text{NaCl} \cdot 2 \text{H}_2\text{O}$	-22.9	75.4
Sodium Bromide	NaBr	-22.9	0.04
Meridianite	$\text{MgSO}_4 \cdot 11 \text{H}_2\text{O}$	-33.3	6.2
Sylvite	KCl	-33.4	1.1
Magnesium chloride dodecahydrate	$\text{MgCl}_2 \cdot 12 \text{H}_2\text{O}$	-36.2	13.5

* Mirabilite reaches a maximum $f_{sm} = 10.5\%$ at -22.9°C but dissolves back at lower temperature (Marion *et al.*, 1999).

Table 2. Main characteristics of the observational data sets used in this work. N is the number of relevant observations available.

Source	ΔT [K]	ΔS [g/kg]	T -range [°C]	S -range [g/kg]	Seawater type	N
Liquidus salinity						
G37	0.1	< 0.1	[−35.5, −1.8]	[32.8, 248.4]	Synthetic	16
NT54*	0.05	< 0.1	[−43.2, −4.4]	[70.8, 237.8]	Pacific	9
DK74	2×10^{-3}	0.02	[−2.2, −0.39]	[6.97, 40.2]	Sargasso Sea	21
B16b	0.1	< 0.1	[−20.6, −1.8]	[35.2, 218.7]	Simplified	18
Mirabilite						
B16a	0.1	n.a.	[−6.4, −22.9]	[34.9, 225.9]	Simplified	n.a.
Liquid H_2O fraction						
RK66	0.5	0.001	[−2, −42]	[10.022, 35.035]	unspecified	23

G37 = *Gitterman* (1937), NT54 = *Nelson and Thompson* (1954), DK74 = *Doherty and Kester* (1974), B16a = *Butler et al.* (2016a), B16b = *Butler et al.* (2016b), RK66 = *Richardson and Keller* (1966)

*Of the *Nelson and Thompson* (1954), only samples with reported SO_4^{2-} concentrations were retained.

Table 3. Liquidus computation methods used in this work.

Label	Computation methods	Reference
A58	$S_{br} = -18.4809 T$	<i>Assur</i> (1958)
NW09	$S_{br} = -21.4 T - 0.886 T^2 - 0.0170 T^3$	<i>Notz and Worster</i> (2009)
POLY3	$S_{br} = -18.7 T - 0.519 T^2 - 0.00535 T^3$	This study (§2.3.1)
CW86	$S_{br} = \alpha_0 + \alpha_1 T + \alpha_2 T^2 + \alpha_3 T^3$	<i>Cox and Weeks</i> (1986)
	$\alpha = [-3.9921, -22.700, -1.0015, -0.019956]$ ($-2 \geq T > -22.9^\circ\text{C}$)	
	$= [206.24, -1.8907, -0.060868, -0.0010247]$ ($-22.9 \geq T > 44^\circ\text{C}$)	
	$= [-4442.1, -277.86, -5.501, -0.03669]$ ($-44 \geq T > -54^\circ\text{C}$)	
mTEOS-10	$\Delta\mu^{TEOS-10}(S_{br}, T) + \mu^c(S_{br}) = 0$	This study (Appendix A)

Table 4. Evaluation of the liquidus curve $S_{br}(T)$ from selected computation methods, by comparison with the observational data (*Gitterman, 1937; Doherty and Kester, 1974; Butler et al., 2016b; Nelson and Thompson, 1954, Table 1*), see Section 2.3.1 for details. The comparison is performed both for the entire temperature range (N=64) and for the TEOS-10 validity range ($T \geq -6^\circ\text{C}$, $S \leq 120$ g/kg, N=29).

Type	Eutectic compliant?	Full T -range				TEOS-10 validity range		
		Bias	RMSE	STDE	ΔS_e [g/kg]	Bias	RMSE	STDE
FREZCHEM	No	1.1	1.9	2.5	3.4	0.08	0.5	1.15
Linear (A58)	No	75.6	75.6	109.3	418.4	1.67	1.80	3.50
3 rd order (NW09)	No	11.7	12.3	29.8	169.5	2.57	2.57	1.26
3 rd order (POLY3)	Yes	-0.4	2.3	3.2	0	-1.33	1.46	1.47
3 rd order piecewise (CW86)	No	1.2	2.9	3.5	-7.1	0.8	1.29	1.67
mTEOS-10	Yes	1.2	3.0	4.6	-0.007	0.04	0.6	1.14

ΔS_e : Difference between predicted $S_{br}(T_e)$ at the assumed eutectic temperature (-36.2°C) and the observational best estimate of the eutectic salinity (250.6146 g/kg). RMSE = Root mean square error, STDE = Standard deviation of error. A58 = *Assur* (1958), NW09 = *Notz and Worster* (2009), POLY3 = 3rd polynomial (eq. 10), CW86 = *Cox and Weeks* (1986), mTEOS-10 = modified TEOS-10 (Section 2.4).

Table 5. Evaluation of liquid H₂O mass fraction (*g/kg*) retrieved from equation (4) with brine mass fraction computed based on equation (3), itself fed by various liquidus salinity and solid salt fraction estimates. Evaluation is performed by comparison with NMR-based estimates (*Richardson and Keller, 1966, N=20*), using the experimentally imposed temperatures and absolute salinities as a basis for computations.

Liquidus	Sol. salt frac.	Liquid frac.	Bias	RMSE	STDE
S_{br}	f_{sm}	ϕ_{br}	g/kg	g/kg	g/kg
FREZCHEM direct estimate of liquid H ₂ O fraction			1.1	8.6	13.3
FREZCHEM	FREZCHEM	n.a.	1.3	8.6	13.4
Linear (A58)	0	n.a.	-28.8	28.9	21.3
3 rd order (NW09)	0	n.a.	6.7	18.05	23.6
3 rd order (POLY3)	0	n.a.	20.3	20.7	19.4
3 rd order (POLY3)	FREZCHEM	n.a.	6.6	10.3	17.5
mTEOS-10	FREZCHEM	n.a.	-0.09	8.9	13.5
3 rd order piecewise (CW86)	n.a.*	CW83	-8.1	10.5	12.4

A58 = *Assur (1958)*; NW09 = *Notz and Worster (2009)*; POLY3 = 3rd order observational fit (eq. 10);

CW86 = *Cox and Weeks (1986)*. CW83 = *Cox and Weeks (1983)*.

* Here eq. 4 is fed directly by brine mass fraction. CW83 originally provide brine volume fraction, which is first converted into liquid mass fraction using eq. 5, using CW86 for liquidus salinity.

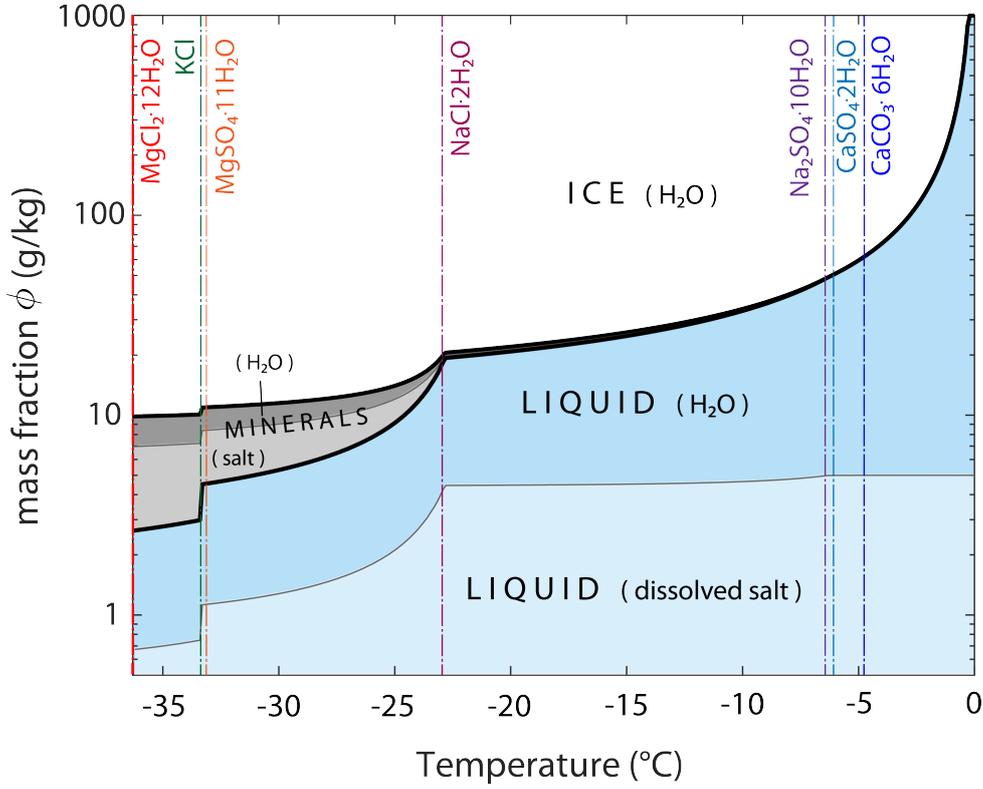


Figure 1. Sea ice phase diagram derived from FREZCHEM outputs, for sea ice with a typical absolute bulk salinity value of $S=5$ g/kg and standard seawater composition (*Millero et al.*, 2008). The mass fraction of the main sea ice constituents (following eq. 7) are shown cumulatively over the $[-36.2, 0^{\circ}\text{C}]$ temperature range. From bottom to top the lines refer to ϕ_{br}^{salt} , $\phi_{br}^{salt} + \phi_{br}^{\text{H}_2\text{O}}$, etc... and so the individual mass fractions are to be read as the vertical interval between the lines. The thick black lines separate individual phases (liquid, minerals, ice), whereas the thin grey lines further split salt and H_2O contributions. Note the logarithmic scale for the y-axis. The supplementary netcdf file includes data for the entire explored salinity range.

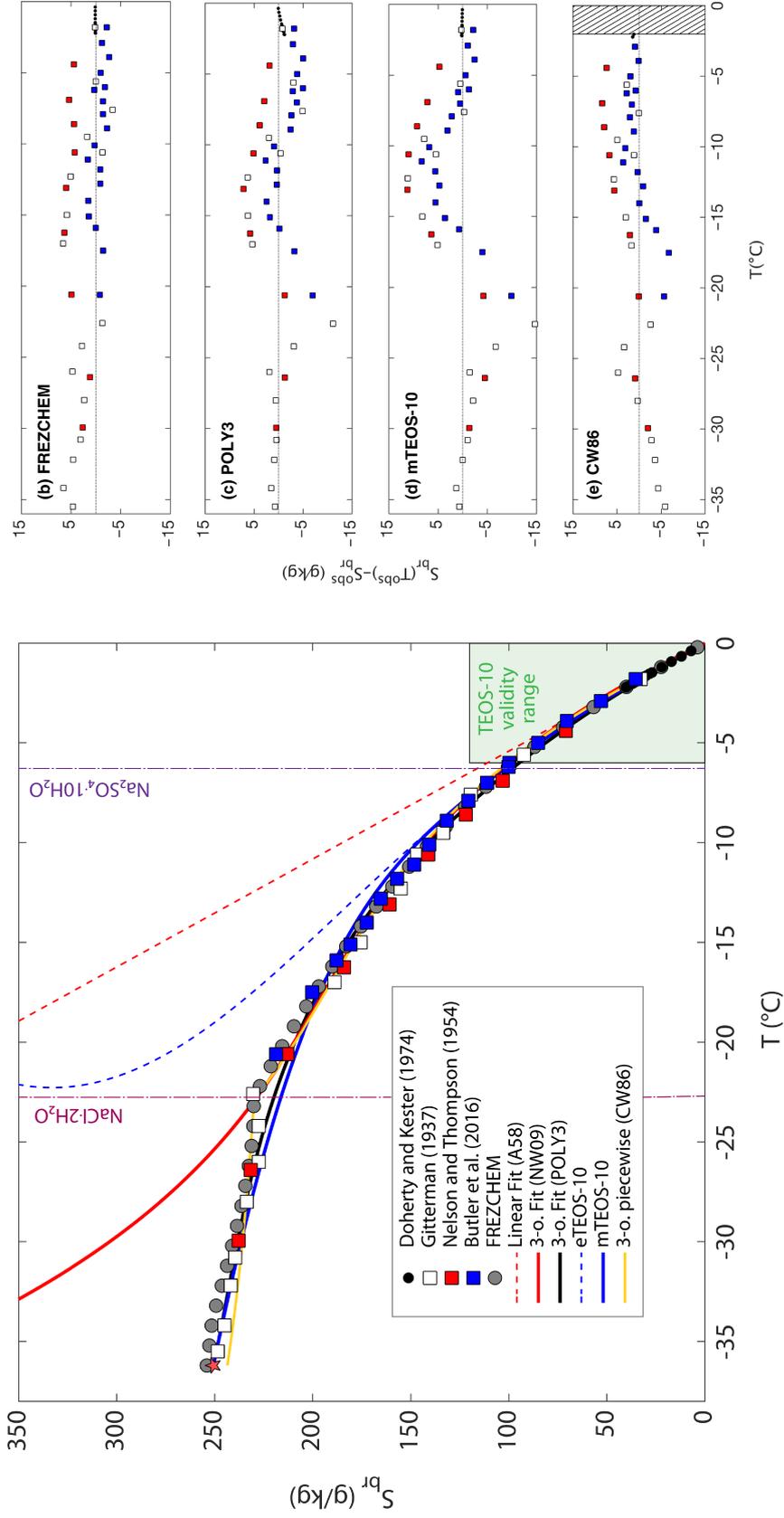


Figure 2. (a) Liquidus salinity as a function of ambient temperature from the Pitzer-Gibbs model (FREZCHEM, grey circles), other computational methods (lines) and observational sources (symbols). The eutectic point is represented by the red star. (b-e) Differences between calculated and observed liquidus salinity for the main computational methods discussed in the text. A58 = Assur (1958), NW09 = Notz and Worster (2009), POLY3 = 3rd polynomial (eq. 10), eTEOS-10 = extended TEOS-10, mTEOS-10 = modified TEOS-10 (Section 2.4), CW86 = Cox and Weeks (1986).

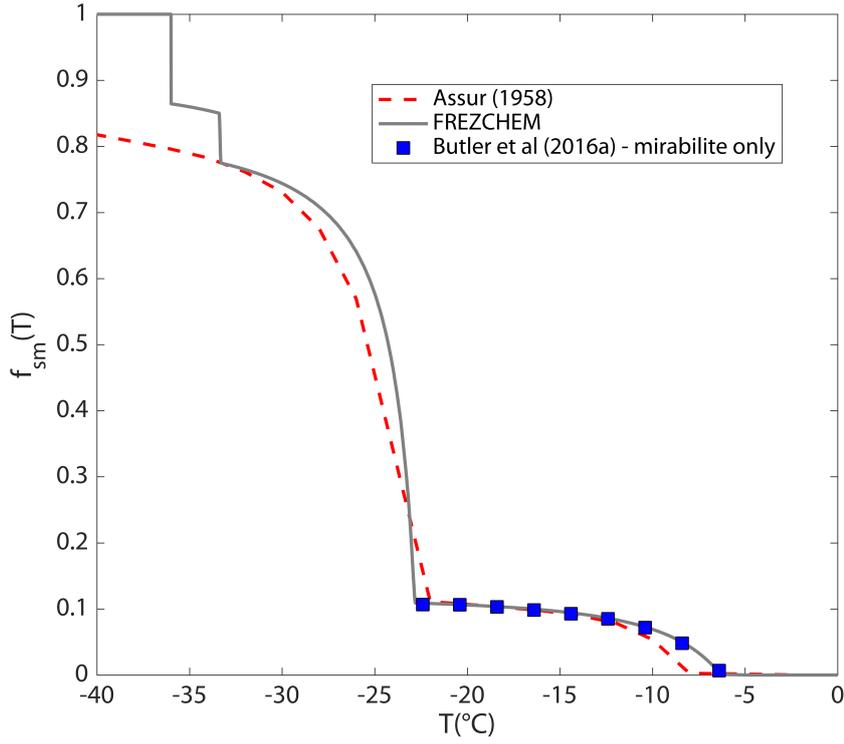


Figure 3. Solid salt fraction f_{sm} derived from FREZCHEM outputs, plotted against (i) the observational fit to the laboratory observations of *Butler et al.* (2016a) (their Table 4, only mirabilite included) and (ii) from the calculations of *Assur* (1958, derived from his Table 3).

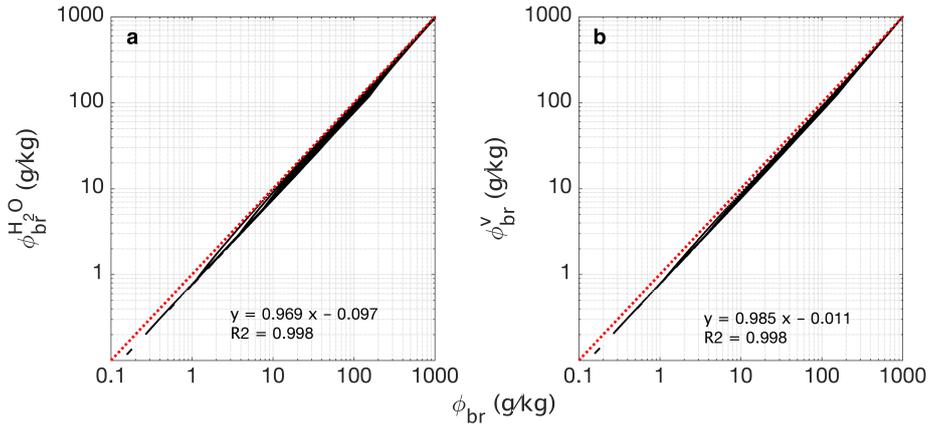


Figure 4. (a) Liquid H_2O mass fraction ($\phi_{br}^{\text{H}_2\text{O}}$) and (b) liquid volume fraction (ϕ_{br}^v) from the 41×363 points of the FREZCHEM outputs, plotted against mass fraction (ϕ_{br}). The red dots give the 1:1 line.

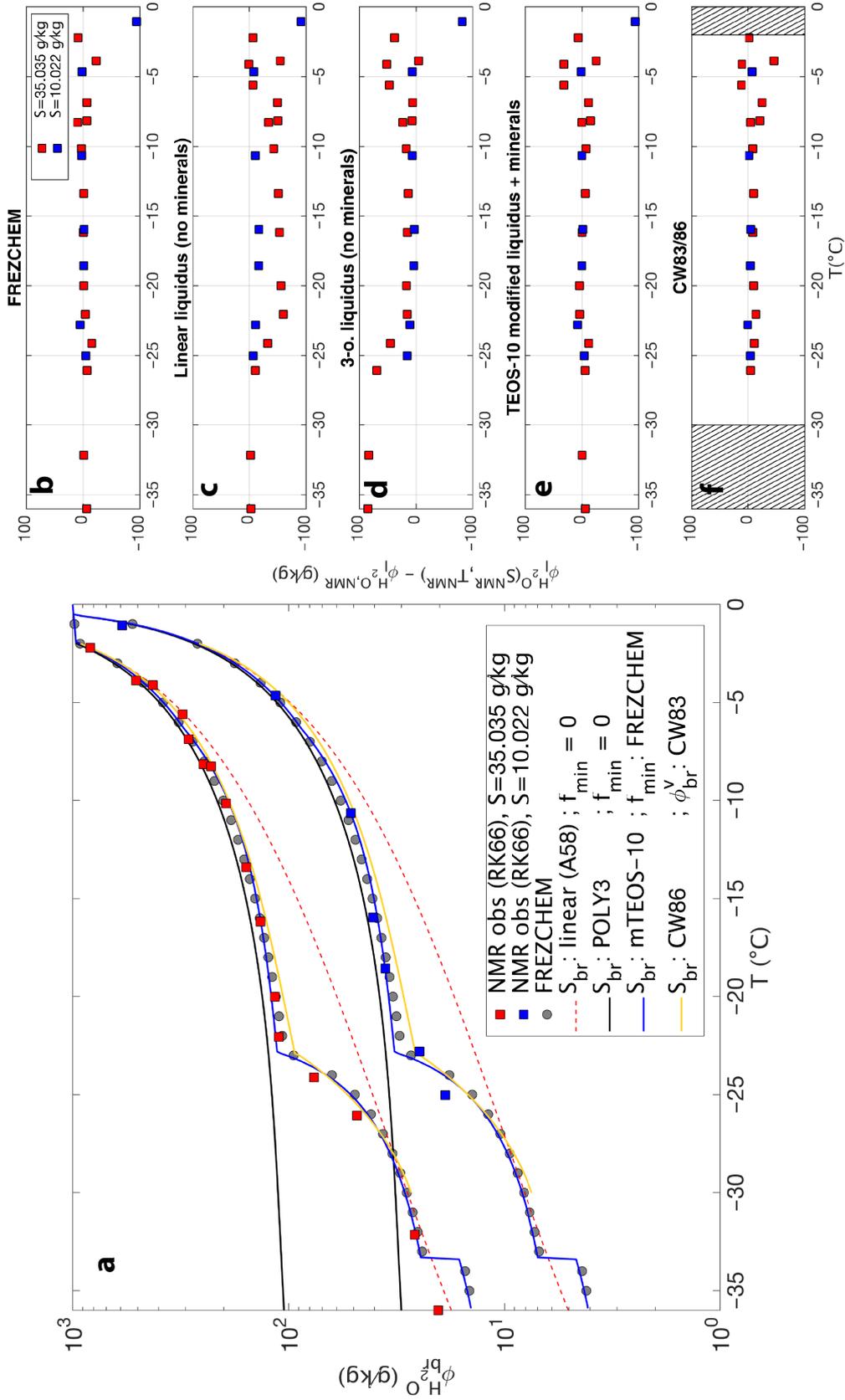


Figure 5. (Left) Liquid H_2O mass fraction as a function of ambient temperature from the Pitzer-Gibbs model (FREZCHEM, grey circles), other computational methods (lines) and digitized Nuclear Magnetic Resonance (NMR) estimates (*Richardson and Keller*, 1966, RK66) (squares, their Figures 2 and 3), at two reference absolute salinities ($S = 10.022, 35.035 \text{ g/kg}$). (Right) Differences between calculated and NMR-derived liquid H_2O fraction estimates from the same sources.

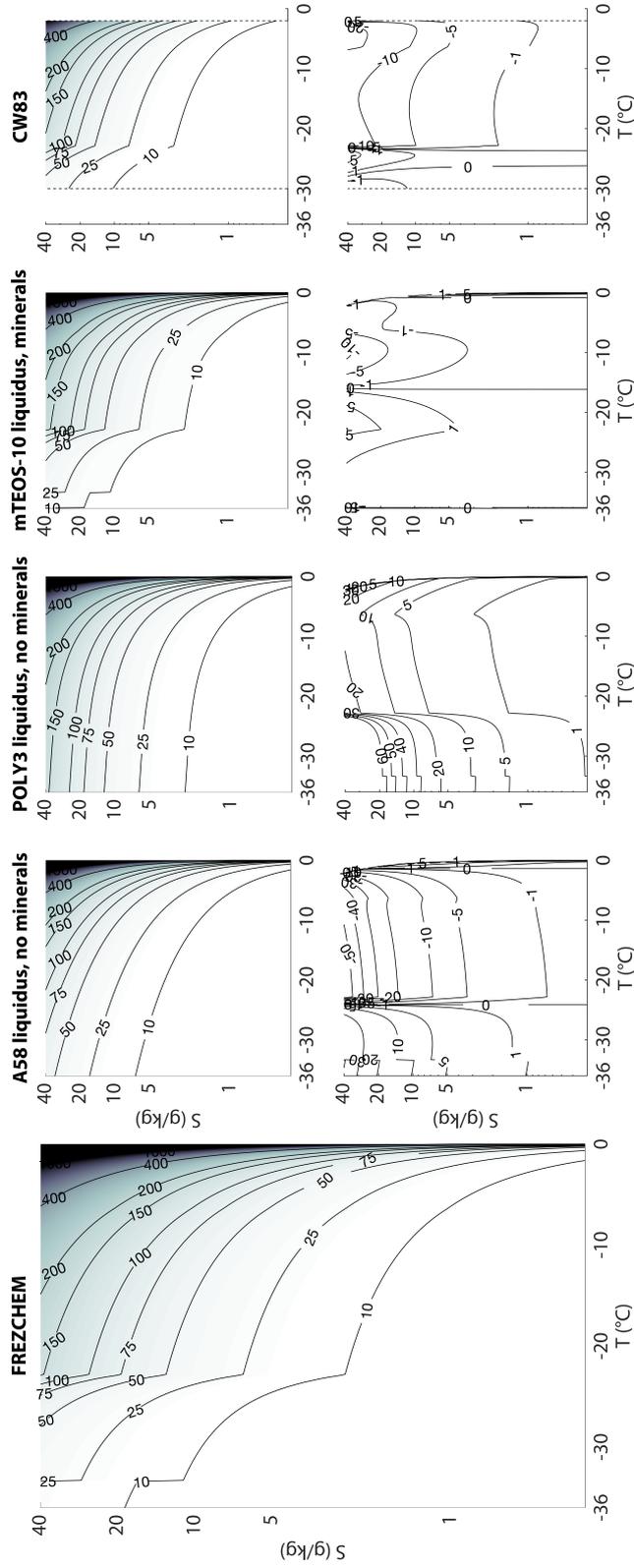


Figure 6. Liquid mass fraction contours in T-S space, derived from FREZCHEM outputs (left panel), from selected computational approaches (top panels), and differences of the latter with FREZCHEM (lower panels). CW83 refers to *Cox and Weeks (1983)* volume fraction converted into mass fraction using equation (5)

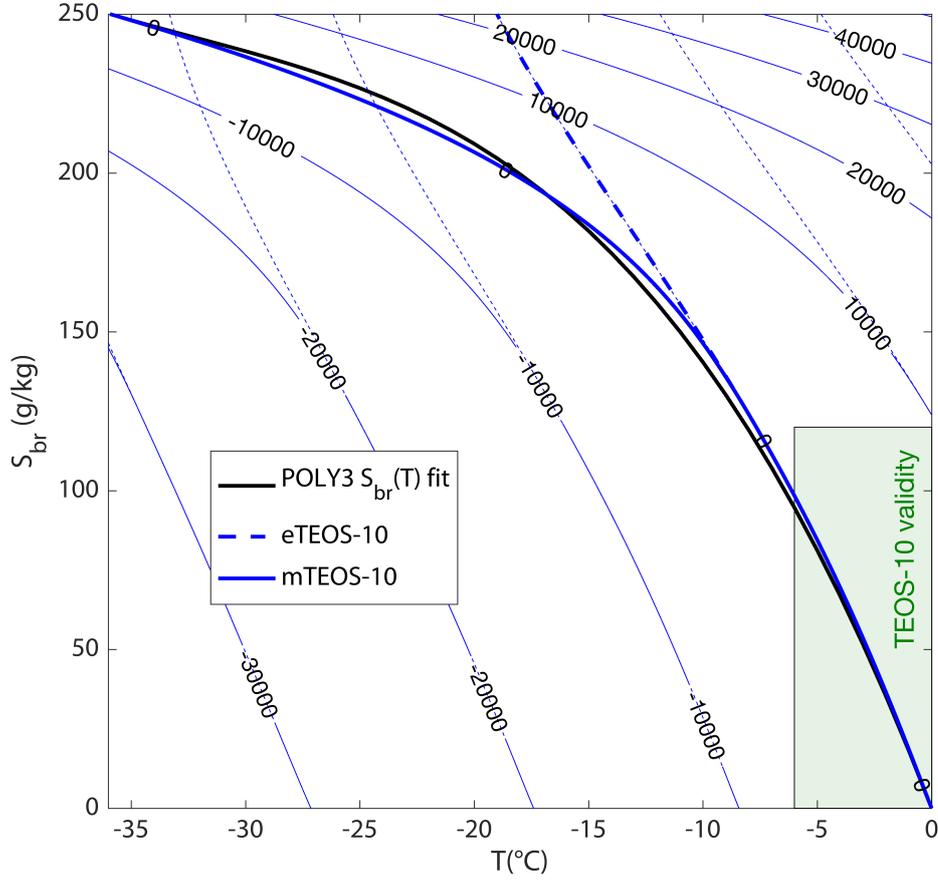


Figure A1. Why TEOS-10 liquidus differs from observations at high salinity and how can this be solved? Liquidus salinities from the POLY3 fit on observations (thick black line), the extended TEOS-10 (thick blue dotted line) and modified TEOS-10 (thick blue line) formulations. The background thin lines contour $\mu^{Th}(T) - \mu^w(S_{br}, T)$ at reference atmospheric pressure using the extended (blue dots) and modified (solid blue) TEOS-10 formulations for the chemical potential of water in salt water. These give a more general context: positive contour values indicate that salt water is more stable than ice, whereas the zero contour corresponds to the liquidus curve.

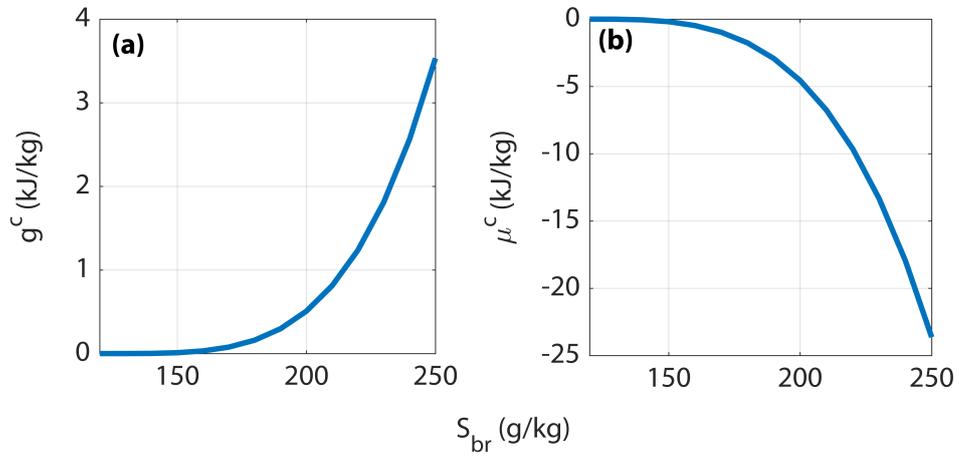


Figure A2. Perturbation functions to the seawater Gibbs free energy $g^c = ax^4$ and to the chemical potential of water in sea water $\mu^c = -3ax^4 - 4aS^0x^3$.

802 **A Appendix: A liquidus curve consistent with TEOS-10**

803 **A.1 Why does using TEOS-10 beyond its limits not work?**

804 Ocean models (e.g. *Madec and the NEMO team*, 2008) have recently been updated
 805 so that their thermodynamic properties – including the freezing temperature of seawater
 806 – all derive from the international thermodynamic equation of seawater (TEOS-10,
 807 *IOC, SCOR and IAPSO*, 2010). Using a fit to retrieve brine salinity as a function of tem-
 808 perature would always somehow conflict with such an approach, leading to inconsisten-
 809 cies between the freezing point of saline inclusions within sea ice and that of the seawater
 810 below.

811 Let us give an example. The freezing temperature T_{fr} obtained from the numer-
 812 ical inversion of the 3rd order fit given by eq. 10 at a salinity of 35 g/kg is -1.978°C .
 813 (The numerical inversion is the most efficient approach we found, reaching a precision
 814 of 10^{-14} °C in a few iterations). At the same absolute salinity of 35 g/kg and at stan-
 815 dard atmospheric pressure, TEOS-10 predicts $T_{fr} = -1.910^{\circ}\text{C}$, that is 0.068°C higher.
 816 The difference is small, but may lead to situations where the ocean would see freezing
 817 seawater, whereas the sea ice model would assume that at such temperature, the medium
 818 should be all liquid. The inconsistency reaches 0.10°C with the *Cox and Weeks* (1986),
 819 and 0.15°C with the *Notz and Worster* (2009) fits.

820 Next to inconsistencies, another argument in support of TEOS-10 is intrinsic qual-
 821 ity. Over its claimed validity range ($T \geq -6^{\circ}\text{C}$, $S < 120$ g/kg), the TEOS-10 derived freez-
 822 ing point and liquidus salinity clearly outperform any other estimate. Indeed, as com-
 823 pared with the observational estimates (Section 2.3.1) lying within the TEOS-10 valid-
 824 ity range ($N = 29$), the TEOS-10 liquidus salinity error is of 0.6 ± 1.1 g/kg, at least
 825 twice as small as any of the usual fits (see Table 4). TEOS-10 not only better fits the
 826 observations of *Doherty and Kester* (1974) over which it was fitted, but also the inde-
 827 pendently acquired data of *Gitterman* (1937) and *Butler et al.* (2016b). There is no re-
 828 tained observation from *Nelson and Thompson* (1954) falling within the TEOS-10 va-
 829 lidity range.

830 Hence, to achieve consistency with ocean models and the best precision near the
 831 freezing point, the best approach to retrieve the liquidus salinity as a function of tem-

832 perature is to invert the TEOS-10 freezing point. However, out of its claimed validity
 833 range, the TEOS-10 freezing point has not been tested, and is by default undefined.

834 One can remove all the TEOS-10 high salinity and low temperature barriers to get
 835 a defined value for T_{fr} out of the claimed TEOS-10 validity bounds (an approach that
 836 we refer to as *extended* TEOS-10, illustrated with the dashed blue curve in Fig. A1). Yet,
 837 doing this brings two other problems. The first one, somehow expected, is that the re-
 838 sulting freezing temperature value rapidly departs from observations at salinities higher
 839 than 120 g/kg. The other problem is worse: the freezing temperature non-monotonically
 840 depends on temperature: the extended TEOS-10 freezing temperature reaches a min-
 841 imum near approximately -22.3°C near $S = 330$ g/kg and then increases back to warmer
 842 temperatures. This non-monotonicity implies that the reciprocal of the TEOS-10 freez-
 843 ing temperature, i.e., the liquidus salinity, is undefined below -22.3°C . For this reason,
 844 the extended TEOS-10 approach is not workable and must be rejected.

845 **A.2 What should be modified in TEOS-10?**

846 The desire to achieve a precise estimate of the liquidus salinity at all temperatures,
 847 fully consistent with ocean models, encouraged us to seek a modification of TEOS-10 that
 848 would ensure a reasonable freezing temperature out of its claimed validity bounds. To
 849 do this, we must first explain how TEOS-10 derives the freezing temperature as a func-
 850 tion of salinity. Let us mention that all salinities are absolute in the TEOS-10 sense, that
 851 temperatures are expressed in Celsius, and that pressure effects are ignored in the fol-
 852 lowing developments.

853 The TEOS-10 approach is based on a complete specification of the state of a unit
 854 mass of seawater by the Gibbs free energy or potential in J/kg. The Gibbs potential is
 855 an extensive variable; and therefore the sea ice Gibbs function g can be written as the
 856 sum of pure ice of Ih crystal type (g^{Ih}) and salt water (g^{sw}) contributions weighted by
 857 brine fraction ϕ_{br} (*Feistel and Hagen, 1998*):

$$g(\phi_{br}, S_{br}, T) = g^{Ih}(T)(1 - \phi_{br}) + g^{sw}(S_{br}, T)\phi_{br}, \quad (\text{A.1})$$

858 a form that assumes a negligible contribution of minerals to the Gibbs function. The TEOS-
 859 10 manual and routines provide exhaustive polynomial developments for the seawater
 860 Gibbs potential g^{sw} (*Feistel, 2008*), and also provide the IAPWS Gibbs potential for ice
 861 Ih , g^{Ih} (*Feistel and Wagner, 2006*). The equilibrium of liquid and solid phases occurs

862 at the minimum of the Gibbs function ($\partial g/\partial\phi = 0$), or equivalently at equal chemical
 863 potentials for pure ice and water in salt water (*Feistel and Hagen, 1998*). The liquidus
 864 curve $S_{br}(T)$ (and the freezing temperature $T_f(S)$) stems from the equality of the chem-
 865 ical potentials and therefore verifies:

$$\Delta\mu(S_{br}, T) \equiv \mu^{Ih}(T) - \mu^w(S_{br}, T) = 0, \quad (\text{A.2})$$

866 where μ^{Ih} and μ^w are the chemical potentials of ice *Ih* and water in salt water, respec-
 867 tively, and $\Delta\mu$ is defined as the difference between both. Using the relations between chem-
 868 ical and Gibbs potentials for ice *Ih* ($g^{Ih} = \mu^{Ih}$) and of water in salt water ($\mu^w = g^{sw} -$
 869 $S \cdot \partial g^{sw}/\partial S$), the freezing condition becomes:

$$\Delta\mu(S_{br}, T) = g^{Ih}(T) - g^{sw}(S_{br}, T) + \left[S \cdot \frac{\partial g^{sw}}{\partial S} \right]_{S_{br}, T} = 0. \quad (\text{A.3})$$

870 It is from this expression of the freezing condition that the TEOS-10 freezing point is
 871 numerically derived, using the IAPWS-06 for g^{Ih} and TEOS-10 for g^{sw} .

872 Fig. A1 depicts the contours of $\Delta\mu$ in $T-S_{br}$ space, based on IAPWS-06 and TEOS-
 873 10 Gibbs potentials. We see that within the claimed validity range of TEOS-10 ($[-6, 40^\circ\text{C}]$,
 874 $[0, 120 \text{ g/kg}]$), the zero contour of $\Delta\mu$ (equivalent to the TEOS-10 freezing point) closely
 875 matches the observation-derived liquidus curve but spreads from it at high salinity. This
 876 mismatch suggests the need to modify the sea ice Gibbs function and the associated chem-
 877 ical potentials in such a way that the zero contour of $\Delta\mu$ gets closer to the observed liq-
 878 uidus curve. We argue that it is TEOS-10 that should be modified, not IAPWS-06, be-
 879 cause the latter has been tested over a much wider temperature range than TEOS-10
 880 and has no salinity dependence anyway.

881 **A.3 Modifying TEOS-10 to improve the freezing point at salinities higher** 882 **than 120 g/kg.**

883 We seek a modification of TEOS-10 modification that achieves two basic require-
 884 ments:

- 885 • to preserve TEOS-10 integrity within its claimed validity range and,
- 886 • to give a liquidus curve in better agreement with observations at high salinity.

887 Such TEOS-10 modification should be done at the most fundamental level, namely by
 888 acting on the Gibbs function. We target the salinity dependency of g , because the lat-

889 ter determines the chemical potential of water in salt water. In addition, S must be the
 890 master independent variable for such operation because the extended TEOS-10 freez-
 891 ing point is not monotonic at high salinity.

892 On these grounds, we propose the following *modified* Gibbs function for salt wa-
 893 ter:

$$g^{sw}(S_{br}, T) = g^{TEOS-10}(S_{br}, T) + g^c(S_{br}), \quad (\text{A.4})$$

894 where $g^c = g^c(S_{br})$ should be constructed such that the freezing condition [eq. A.3] fits
 895 the freezing temperature data $T_f^n(S_A^n)$, with $n=1, \dots, 31$. To preserve TEOS-10 integrity,
 896 we only use the 31 data points in the ranges $S > 120$ g/kg and $T > -36.2^\circ\text{C}$.

897 In order to derive a fitting function, we impose the freezing condition (eq. A.3) to
 898 hold along the expected freezing temperature $T_f(S_{br})$ curve. Re-expressing in terms of
 899 g^c , we get:

$$\mu^c \equiv g^c - S \cdot \frac{\partial g^c}{\partial S_{br}} = \Delta\mu^{TEOS-10}[S_{br}, T_f(S_{br})]. \quad (\text{A.5})$$

900 where the right-hand side, only a function of S_{br} , is evaluated using the IAPWS-06 and
 901 extended TEOS-10 Gibbs potentials (unperturbed) for ice Ih and salt water. $\Delta\mu^{TEOS-10}$
 902 is evaluated at the sought freezing point, not at the predicted freezing point, hence $\Delta\mu^{TEOS-10} \neq$
 903 0. μ_c can be seen as the perturbation applied to the *TEOS-10* chemical potential of
 904 water in salt water $\mu^w = \mu^{w,TEOS-10} + \mu^c(S_{br})$.

905 Now, as a practical matter, we want to only add this correction to the TEOS-10
 906 Gibbs function when the absolute salinity is greater than the upper limit of the range
 907 of validity of the TEOS-10 Gibbs function, namely when $S_{br} > S_0 = 120$ g/kg. Let
 908 us define

$$x = S_{br} - S_0, \quad (\text{A.6})$$

909 and we will seek a functional form for g^c as a polynomial in x . The freezing condition
 910 reads:

$$g^c - (x + S_0) \cdot \frac{\partial g^c}{\partial x} = \Delta\mu^{TEOS-10}(x) \quad (\text{A.7})$$

911 We impose the two additional constraints:

$$\begin{aligned} g^c(x \leq 0) &= 0, \quad (\text{TEOS-10 integrity}), & (\text{A.8}) \\ \left[g^c - (x + S_0) \cdot \frac{\partial g^c}{\partial x} \right]_{x_e=S_e-S_0} &= \Delta\mu[S_e, T_e(S_e)], \quad (\text{Eutectic compliance}), \end{aligned}$$

912 with $S_e = 250.6146$ g/kg and $T_e = -36.2^\circ\text{C}$ are the eutectic salinity and tempera-
 913 ture, respectively. On these grounds, one can fit a freezing point function $g^c(S)$ that sat-

914 isfies the two constraints and minimizes the least-square difference between μ^c and $\Delta\mu(S^n, T_f^n)$,
 915 $n=1-31$ (see Fig. S1 for an example). From μ_c , a *modified* TEOS-10 freezing point can
 916 then be obtained by solving $\mu_w[S_{br}, T_f(S_{br})] = \mu_i[T_f(S_{br})]$, and the liquidus curve $S_{br}(T)$
 917 can be retrieved by numerical inversion.

918 We tried several forms for the Gibbs perturbation function g^c . For instance, we tried
 919 $g^c(x) = ax^2 + bx^3 + cx^4$, and computed the coefficients by minimizing the square dif-
 920 ference between μ^c and $\Delta\mu$ and ensuring that the two constraints [A.8] were respected,
 921 giving a liquidus curve in very good agreement with observations ($\Delta S_{br} = 2.8 \pm 4.4$
 922 g/kg). Relieving the eutectic compliance implies a lower brine salinity bias overall, but
 923 implies errors on eutectic temperature of about 3°C.

924 The most convenient expression we could find takes the following quartic form:

$$g^c(x) = a \cdot x^4, \quad a = 1.2370 \times 10^{-5} \text{ J/kg}/(\text{g}^4/\text{kg}^4) \quad (\text{A.9})$$

925 depicted in Fig. A2 (together with the chemical potential perturbation function). The
 926 quartic form does virtually as well ($\Delta S_{br} = 3.0 \pm 4.6$ g/kg) as more complicated at-
 927 tempts. Such quartic expression is convenient for several reasons. First it is simple. Sec-
 928 ond, the coefficient a does not need to be fitted, it rather directly derives from the eu-
 929 tectic compliance condition. Third, the S_{br} derivatives of the full Gibbs function are con-
 930 tinuous up to order 3 at $x = 0$. g^c changes the freezing condition in a way that appro-
 931 priately curves the freezing point function ($\Delta\mu = 0$ isoline) at high salinities (Fig. A1).